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(56) Documents Cited

|                      |                      |                      |
|----------------------|----------------------|----------------------|
| <b>EP 0430818 A1</b> | <b>EP 0387997 A1</b> | <b>EP 0383482 A1</b> |
| <b>EP 0383480 A1</b> | <b>EP 0217732 A1</b> | <b>US 5368767 A</b>  |
| <b>US 4897212 A</b>  | <b>US 4750942 A</b>  | <b>US 3255117 A</b>  |

(58) Field of Search

**UK CL (Edition S ) C1J JXX , C5D DEX DHE DHZ**  
**INT CL<sup>7</sup> C11D 7/20**  
**ONLINE: EPODOC, WPI, JAPIO**

(54) Abstract Title

**Dishwashing compositions comprising ceramics**

(57) Use of a ceramic composition to protect glassware from corrosion, the ceramic composition being made using at least one compound which releases an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion.

Preferred 'ceramics' include oxides of zinc aluminium, tin magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum or precursors thereof.

GB 2 361 708 A

CERAMIC DISHWASHING COMPOSITION

The invention relates to a new type of use for a ceramic composition to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher, compositions intended for use in a dishwasher for the aforesaid purpose and a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher.

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The problem of glassware corroding during washing and/or rinsing cycles of a dishwasher has long been known. Current opinion is that the problem of corrosion in glassware is the result of two separate phenomena. On the one hand, the corrosion is clearly due to minerals from the glass composition accompanied by hydrolysis of the silicate network. On the other hand, silicate material is released from the glass. After several washes in a dishwasher, both phenomena can cause damage to glassware such as cloudiness, scratches, streaks and similar.

Silicate compounds are known to be effective in preventing minerals from being released from the glass composition but on the other hand can tend to increase the separation of silicate material at the surface of the glass.

Various proposals have been put forward as a means of dealing with the problems described above.

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One approach is to use zinc, either in metallic form (US Patent No. 3,677,820) or in the form of zinc compounds. The use of soluble zinc salts as a means of preventing the corrosion of glassware in dishwasher  
5 cleansers is described in US Patent No. 3,255,117, for example.

Because of a number of disadvantages inherent in using soluble zinc salts (in particular the formation of  
10 a precipitate of insoluble zinc salts with other ions in the washing or rinsing water), European patent applications EP 0 383 480, EP 0 383 482 and EP 0 387 997 propose the use of insoluble zinc compounds as a means of inhibiting corrosion of glassware in automatic  
15 dishwashers. Specifically, the insoluble zinc salts proposed are zinc silicate, zinc carbonate, zinc oxide, basic zinc carbonate (approximately:  $\text{Zn}_2(\text{OH})_2\text{CO}_3$ ), zinc hydroxide, zinc oxalate, zinc monophosphate ( $\text{Zn}_3(\text{PO}_4)_2$ ) and zinc pyrophosphate ( $\text{Zn}_2(\text{P}_2\text{O}_7)$ ). If using zinc salts  
20 of this type in granular cleansing compounds, the insoluble zinc compound is specified as having a maximum particle size of less than 1.7 mm (EP 0 383 482), whilst a mean particle size of less than 250  $\mu\text{m}$  is specified for the insoluble zinc compound used in a liquid dishwasher  
25 compound - (EP 0 383 480 and EP 0 387 997).

The disadvantage of the prior art essentially resides in the fact that, because the zinc compounds are not readily soluble or are insoluble, it is difficult to  
30 ensure that a sufficient quantity of active agent will be present in the washing or rinsing liquid to protect glassware from corrosion. Furthermore, in view of the

high specific density of the insoluble zinc compounds listed, problems of separation arise with powdered mixtures or settlement in the case of liquid mixtures. Finally, all of the known compositions are intended to be  
5 active during only one specific stage of the washing cycle, i.e. if admixed with a granular cleanser composition during the washing cycle or if admixed with a liquid rinsing composition with the rinsing cycle. None of the known compositions has the capacity to become and  
10 remain active starting from the washing cycle and/or one of the intermediate rinsing cycles onwards.

The underlying objective of the present invention is to resolve one but preferably all of the existing  
15 problems outlined above.

This objective is achieved by the invention due to the use of a ceramic composition to protect glassware from corrosion, the ceramic composition being made using  
20 at least one compound which releases an active anti-corrosion agent during the washing and/or rinsing cycles of a dishwasher.

By preference, the compound(s) which release(s) an  
25 active agent to prevent corrosion during washing and/or rinsing cycles of a dishwasher is/are from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum and/or precursors  
30 thereof.

In one specific embodiment, the invention proposes that at least one of the compounds used should be zinc oxide and/or a precursor thereof.

5 By preference, the ceramic composition is used in tablet form.

Alternatively, the ceramic composition is used in crushed form, and more preferably in ground form.

10

The ground ceramic composition preferably has an average particle size of at most 500  $\mu\text{m}$ .

The invention also relates to a composition for use  
15 in a dishwasher which contains an active quantity of a ceramic composition in crushed form to protect glassware against corrosion, the ceramic composition being made using at least one compound which releases an active agent to protect glassware from corrosion during washing  
20 and/or rinsing cycles of a dishwasher.

The ceramic composition is preferably used in ground form, more preferably with a mean particle size of at most 500  $\mu\text{m}$ .

25

The composition proposed by the invention preferably contains the crushed ceramic composition in a quantity of from 0.1 to 10.0% by weight, more preferably in a quantity of from 0.5 to 5.0% by weight.

30

The invention also relates to a composition for use in a dishwasher in the form of a tablet containing an

active quantity of a ceramic composition to protect glassware against corrosion, the ceramic composition being made using at least one compound which releases an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion.

In one embodiment, the invention proposes that the compound(s) which release(s) an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher should be selected from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium, manganese and/or lanthanum.

In one particular embodiment, the invention proposes that at least one of the compounds should be zinc oxide and/or a precursor thereof.

Finally, the invention relates to a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher, characterised in that the glassware is brought into contact with washing or rinsing water containing an active quantity of the aforesaid composition containing a crushed ceramic composition.

Alternatively, a method of inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher is proposed, in which the composition described above containing the ceramic composition is provided in tablet form, placed in the interior of the

dishwasher at a point which is accessible to the washing and/or rinsing water.

Before giving a detailed explanation of the features  
5 and advantages of the present invention, it should be pointed out that for the purpose of the present invention, the concept "ceramic composition" should be construed in its broadest sense, namely all materials made up of inorganic and predominantly non-metallic  
10 compounds or elements that are crystalline by reference to more than 30% by volume, in particular - but not restricted to - clay ceramic substances but also glass ceramic substances, for example.

15 The present invention solves at least one, and in preferred embodiments all the problems inherent in the prior art described above.

By using a ceramic substance as a "base" for one or  
20 more reagents to protect glassware from corrosion in a dishwasher, the problem caused by the extensive formation of precipitate from insoluble salts which result in an undesirable deposit, such as occurs with the prior art due to the use of soluble zinc salts for this purpose,  
25 are avoided. Instead, the active agents, such as zinc ions, are released from the ceramic compound proposed by the invention into the washing or rinsing water in a delayed release pattern but are not present in a high enough concentration to lead to an extensive and  
30 undesirable formation of insoluble salts. The disadvantages of using insoluble zinc compounds described

above are avoided by using the ceramic compositions proposed by the invention.

By using the ceramic composition proposed by the invention in ground form as an additive to standard dishwasher products, which are generally made as powders or liquids, the problem of separation described above is also resolved since the use of a ceramic composition offers greater flexibility in terms of adjusting the specific density to requirements.

If the ceramic composition proposed by the invention is provided in tablet form and placed in the interior of the dishwasher at a point which is accessible to the washing and/or rinsing water, e.g. in the cutlery basket, it will also provide, for the first time ever, active protection against corrosion throughout all washing and rinsing cycles, i.e. from the pre-rinse cycle through to the cleaning cycle and then the intermediate rinse cycles through to the final rinse cycle and, what is more, will last for several cycles. As a result, not only is glassware thoroughly protected against corrosion in the dishwasher, handling is made significantly easier and more convenient for the consumer.

25

If the ceramic composition proposed by the invention is used in crushed form, it may be ground in a grinder specifically suited to this purpose, for example, and an appropriate fraction of particles separated out, e.g. having an average grain particle of at most 500  $\mu\text{m}$ .

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The features of the invention disclosed in the description above and in the claims may be used individually or in any combination to apply the invention in its different embodiments.

5

The invention will now be described with reference to the following examples.

**Example 1**

10 In this example a ceramic material with the composition of Table I was prepared using the process described below:

Table 1

| Component                     | Mol % |
|-------------------------------|-------|
| P <sub>2</sub> O <sub>5</sub> | 24    |
| Na <sub>2</sub> O             | 27    |
| SiO <sub>2</sub>              | 25    |
| ZnO                           | 24    |

15 Process of preparation:

45 g Na<sub>3</sub>PO<sub>4</sub> anhydrous, 63 g NaH<sub>2</sub>PO<sub>4</sub> , 21 g SiO<sub>2</sub> and 77 g Zr<sub>3</sub>PO<sub>4</sub> all anhydrous were homogeneously mixed and wetted with a small amount of water during steadily kneading of the mixture until a dough like plastic mass is obtained. The mass is left to stand for 2 hours at 30

20

°C during which time the mass swells due to the development of gas inside. The body is kneaded again to eliminate the gas and close the pores. The resulting mixture is fed into the die of a press machine having a rectangular cross-section of 8 x 8 cm<sup>2</sup>. The mixture was pressed to obtain a block. The block dries in between 12 hours at 35 °C to a solid block.

The block was then placed in an electric oven, which was heated up to 150°C at a speed of 50°C/hour. Once the temperature of 150°C is reached the heating rate is increased to 180 °C/hour until a temperature of 780 °C is reached and this temperature is then maintained for 24 hours. After this period the oven is brought back to room temperature at a rate of 180°C/hour.

15

Example 2Table 2

| Component                     | Mol % |
|-------------------------------|-------|
| P <sub>2</sub> O <sub>5</sub> | 25    |
| Na <sub>2</sub> O             | 30    |
| SiO <sub>2</sub>              | 15    |
| ZrO <sub>2</sub>              | 10    |
| CaO                           | 20    |

The preparation, processing, forming and sintering of this composition was made following the same process explained for Example 1.

Example 3

Comparative tests on the glass-protecting performance of the composition of Example 1 were performed as explained below.

5 Pieces of glassware were washed 50 and 100 times in a dishwashing machine (Miele G540) using for each cleaning cycle 20 g of the commercial dishwashing detergent "Calgonit Ultra 2-Phases Powder" and setting the machine to a program running at a 65°C in the washing  
10 cycle and at 65°C in the rinsing cycle. The water hardness in the dishwashing machine was set to be 0,1°dGH and the average water consumption per wash was 23,5 l. In the rinsing cycle the machine was set to use 3 ml of the commercial rinse aid "Calgonit Klarspüller".

15 The pieces of glassware used for the test were as follows:

Luigi Bormioli (Italy):

" linea Michelangelo David" Cl80, Stemglass, crystal glass

20 Verrerie Cristallerie D'Arques (France):

"Luminarc Octime Transparent", Whiskeyglass 30cl

"Longchamp" 17 cl; Stemglass, lead crystal glass

"Luminarc Islande Dauphine", 33 cl, decorated longdrinkglass

25 Ruhr Kristall Glas (Germany):

"Kölner Stange" ,24 cl, beer glass

New pieces of glassware were used for the test and each was weighted before the test started. After 50 or 100 complete washing cycles the pieces of glassware were removed from the dishwasher and their weight loss was  
 5 determined gravimetrically.

Additionally the pieces of glassware were visually examined by a panel of trained people in two different environments: at daylight conditions and in a light chamber measuring 70 cm x 40 cm x 65 cm whose interior is  
 10 covered with a matt black coating and which is illuminated with an Osram L20W25S lamp.

The results of the visual examination were recorded using the following scale:

| Value | Evaluation at daylight          | Evaluation in light chamber |
|-------|---------------------------------|-----------------------------|
| 0     | No change                       | No change                   |
| 1     | No visible cloudiness           | Slight cloudiness           |
| 2     | Few visible cloudiness          | Considerable cloudiness     |
| 3     | Considerable visible cloudiness | Strong cloudiness           |
| 4     | Strong cloudiness               | -----                       |

15        The results on glass corrosion of the glassware when no special glass-protecting composition is used are recorded under the heading "Reference". The results obtained when the ceramic composition prepared in Example 1 was placed in the interior of the dishwashing machine at  
 20 the start of the test are recorded under the heading "Ceramic".

Gravimetric determination of glass corrosion

|                | 50 cycles |         | 100 cycles |         |
|----------------|-----------|---------|------------|---------|
|                | Reference | Ceramic | Reference  | Ceramic |
| Glassware type |           |         |            |         |
| Michelangelo   | 41        | 13      | 80         | 28      |
| Oetime         | 20        | 8       | 38         | 20      |
| Longchamp      | 62        | 20      | 125        | 44      |
| RKL Kölsch     | 25        | 5       | 44         | 14      |
| Islande-Dekor  | 378       | 205     | 625        | 398     |

Visual determination of glass damages

|               | 50 cycles |         | 100 cycles |         |
|---------------|-----------|---------|------------|---------|
|               | Reference | Ceramic | Reference  | Ceramic |
| Michelangelo  | 2,5       | 1       | 3,5        | 1,5     |
| Oetime        | 2         | 0,5     | 3          | 1,5     |
| Longchamp     | 3         | 1       | 3,5        | 1,5     |
| RKL Kölsch    | 2         | 1       | 3          | 1,5     |
| Islande-Dekor | 2,5       | 1       | 3,5        | 2       |

5        The results from the preceding tables clearly show that the use of the ceramic compositions of the invention substantially reduces the corrosion of glassware when repeatedly washed in a dishwashing machine.

Claims

1. Use of a ceramic composition to protect glassware from corrosion, the ceramic composition being made using  
5 at least one compound which releases an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher.
2. Use as claimed in claim 1, characterised in that the  
10 compound(s) which release(s) an active agent to protect glassware from corrosion during washing and/or rinsing cycles of a dishwasher is/are selected from the group consisting of oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon, titanium, zirconium,  
15 manganese and/or lanthanum and/or precursors thereof.
3. Use as claimed in claim 2, characterised in that at least one of the compounds is zinc oxide and/or a precursor thereof.  
20
4. Use as claimed in one of the preceding claims, characterised in that the ceramic composition is used in tablet form.
- 25 5. Use as claimed in one of claims 1 to 3, characterised in that the ceramic composition is used in crushed form.
6. Use as claimed in claim 5, characterised in that the  
30 ceramic composition is used in ground form.

7. Use as claimed in claim 6, characterised in that the ground ceramic composition has an average particle size of at most 500  $\mu\text{m}$ .

5 8. Composition for use in a dishwasher, characterised in that it contains an active quantity of a ceramic composition in ground form to protect glassware from corrosion, the ceramic composition being made using at least one compound which releases an active agent during  
10 washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion.

9. Composition as claimed in claim 8, characterised in that the ceramic composition is provided in ground form.

15

10. Composition as claimed in claim 9, characterised in that the ground ceramic composition has an average particle size of at most 500  $\mu\text{m}$ .

20 11. Composition as claimed in one of claims 8 to 10, characterised in that the crushed, ceramic compound is present in a quantity of from 0.1 to 10.0 by weight.

12. Composition as claimed in claim 11, characterised in  
25 that the crushed ceramic compound is present in a quantity of from 0.5 to 5.0% by weight.

13. Composition for use in a dishwasher, characterised in that it contains an active quantity of a ceramic  
30 composition in tablet form to prevent the corrosion of glassware, the ceramic composition being made using at least one compound which releases an active agent during

washing and/or rinsing cycles in a dishwasher to protect glassware from corrosion.

14. Composition as claimed in one of claims 8 to 13,  
5 characterised in that the compound(s) which release(s) an active agent during washing and/or rinsing cycles of a dishwasher to protect glassware from corrosion is/are selected from the group consisting of the oxides of zinc, aluminium, tin, magnesium, calcium, strontium, silicon,  
10 titanium, zirconium, manganese and/or lanthanum.

15. Composition as claimed in claim 14, characterised in that at least one of the compounds is zinc oxide and/or a precursor thereof.

15

16. Method for inhibiting the corrosion of glassware during washing and/or rinsing cycles of a dishwasher, characterised in that the glassware is brought in to contact with washing and/or rinsing water containing an  
20 active quantity of a composition as claimed in one of claims 8 to 12 or 14 to 15, as dependent on one of claims 8 to 12.

17. Method of inhibiting the corrosion of glassware  
25 during washing and/or rinsing cycles of a dishwasher, characterised in that a composition as claimed in claim 13 or 14 and 15, as dependent on claim 13, is placed in the interior of the dishwasher at a point accessible to the washing and/or rinsing water.

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Application No: GB 0105217.4  
Claims searched: 1-17

Examiner: J. P. Bellia  
Date of search: 22 August 2001

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.S): C1J (JXX); C5D (DEX, DHE, DHZ)

Int Cl (Ed.7): C11D 7/20

Other: ONLINE: EPODOC, WPI, JAPIO

### Documents considered to be relevant:

| Category | Identity of document and relevant passage   | Relevant to claims              |
|----------|---|---------------------------------|
| X        | EP 0430818 A1 (COLGATE-PALMOLIVE) See Examples & page 4 line 40-page 5 line 49                    | 1, 2, 5-12<br>14 & 16           |
| X        | EP 0387997 A1 (PROCTER & GAMBLE) See Examples   | 1-3                             |
| X        | EP 0383480 A1 (PROCTER & GAMBLE) See page 6 line 35 - page 8 line 48                              | 1-3, 5-12<br>& 14-16            |
| X        | EP 0383482 A1 (PROCTER & GAMBLE) See Examples especially Example II                               | 1, 2, 5-12<br>& 14-16           |
| X        | EP 0217732 A1 (ALMACA BIOPRODUKTE) See Beispiel 1-3 & WPI abstract Accession No. 1986-239713 [37] | 1, 2, 5-9<br>11, 12, 14<br>& 16 |
| X        | US 5368767 (DONKER <i>et al</i> ) See column 1 line 45-62 & Examples                              | 1, 2                            |
| X        | US 4897212 (KRUSE <i>et al</i> ) See Examples   | 1, 2, 4,<br>13, 14, 16<br>& 17  |
| X        | US 4750942 (van DIJK <i>et al</i> ) See Examples  | 1, 2                            |

|   |   |   |  |
|---|---|---|--|
| X | Document indicating lack of novelty or inventive step   | A | Document indicating technological background and/or state of the art.  |
| Y | Document indicating lack of inventive step if combined with one or more other documents of same category. | P | Document published on or after the declared priority date but before the filing date of this invention.          |
| & | Member of the same patent family  | E | Patent document published on or after, but with priority date earlier than, the filing date of this application. |



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**Application No:** GB 0105217.4  
**Claims searched:** 1-17

**Examiner:** J. P. Bellia  
**Date of search:** 22 August 2001

| Category | Identity of document and relevant passage     | Relevant to claims         |
|----------|---|----------------------------|
| X        | US 3255117 (KNAPP <i>et al</i> ) See Examples | 1, 2, 5-9, 11, 12, 14 & 16 |

|   |   |   |  |
|---|---|---|--|
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| & | Member of the same patent family  | E | Patent document published on or after, but with priority date earlier than, the filing date of this application. |